Reunión Ibérica de Adsorción

XXXII RIA

LIBRO DE ACTAS

22-24 Septiembre, 2008

Universidad Rey Juan Carlos
Campus de Móstoles
Madrid

ISBN: 978-84-691-5383-3

Depósito Legal:

Diseño y producción: PIXEL Creación y Producción Gráfica, S.L.
Tel.: 914 503 249

Edición: Jesús Mª Arsuaga

UPGRADING OF THE LIGHT NAPHTHA FRACTION WITH ZEOLITE BETA

Patrick S. Bárcia[1], Marco P.M. Nicolau[1], José A.C. Silva[1], Alírio E. Rodrigues[2]

[1] Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Bragança, Apartado 1134, 5301-857 Bragança, Portugal.

[2] Laboratory of Separation and Reaction Engineering, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua do Dr. Roberto Frias, S/N 4200-465 Porto, Portugal.

Summary

Multicomponent adsorption of alkanes in the C_5-C_6 range was investigated in a sample of zeolite BETA. 6-components breakthrough experiments were performed showing interesting properties for the separation of the light naphtha fraction. The lower adsorption enthalpy of C_5 alkanes was explored by a temperature sensibility analysis demonstrating that at 583 K C_5/C_6 equimolar mixture can be separated in a single step into low and high octane number (RON) fractions. The separation 23DMB/3MP can not be achieved in the case of mixtures with the typical composition of the isomerization products, but zeolite BETA still selective for 22DMB resulting in a slight increase of the RON comparatively to the final isomerate from the conventional processes.

Introduction

The oil price climbing stresses the demand for more efficient refining processes capable to produce high quality gasoline fulfilling at the same time the environmental restrictions imposed to the use of additives as octane enhancers. The light naphtha fraction used for the production of gasoline generally contains a significant amount of low RON molecules such as *n*-pentane (nPEN) and *n*-hexane (nHEX). These linear alkanes can be successfully removed from the light naphtha thanks to the isomerization processes developed along the last decades by IFP and UOP. These processes consist in converting linear alkanes into their high RON branched isomers by incomplete catalytic reaction in Pt supported on chlorinated alumina or H-mordenite, followed by the separation of the non-converted linear molecules in an adsorber packed with zeolite 5A (see Figure 1a). However, the final isomerate still containing more than 36% of low RON linear and monobranched alkanes as shown in Figure 1b.

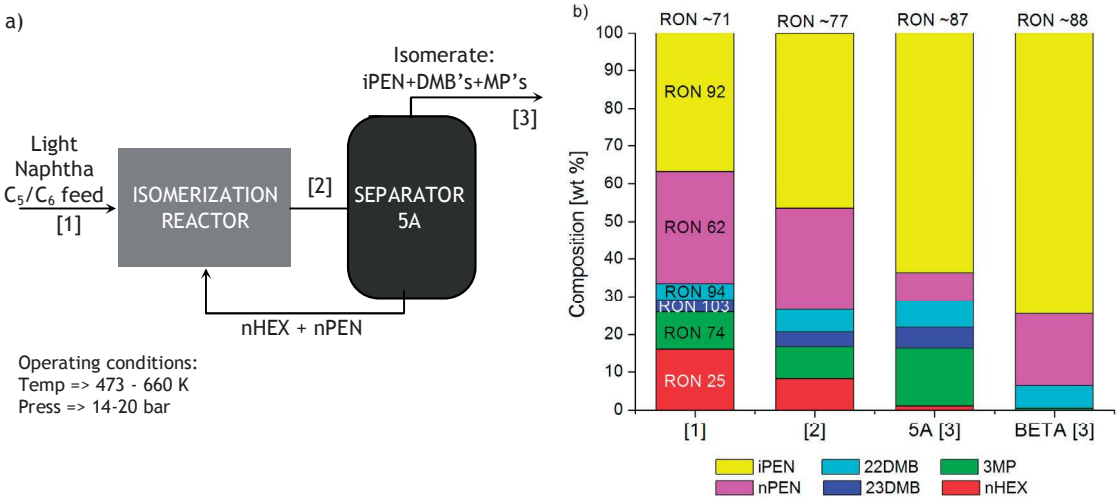

Figure 1. a) Simplified scheme of a conventional isomerization process with recycle, b) Typical composition of the stream in the different stages of the isomerization process[2].

It was demonstrated in a previous work that zeolites BETA can be an effective adsorbent to separate monobranched from dibranched C_6 isomers[1]. However, experimental data published in the literature for adsorptive separation are often limited to binary or ternary equimolar cases which hardly represent the complexity of the real operating conditions existing in the refining process. The aim of this work is to demonstrate the behaviour of a simulated light naphtha fraction in fixed bed packed with zeolite BETA.

Experimental procedure

Breakthrough experiments in vapour phase with mixtures of nHEX, 3-methylpentane (3MP), 2,3-dimethylbutane (23DMB), 2,2-dimethylbutane (22DMB), nPEN and *i*-pentane (iPEN) were performed in zeolite BETA pellets. The adsorption column was operated by introducing continuously a known composition of C_6 isomers in Helium stream. The concentration history at the outlet of the packed bed is measured in order to collect samples during the breakthrough experiment. After the saturation is reached, the composition of each sample loop is evaluated in a proper chromatographic column.

Results and discussion

The effect of the temperature in the breakthrough curves of a 6-component equimolar mixture are shown in Figure 2a-b. The breakthrough profiles show a separation between 3MP and the dibranched C_6 isomers which is acceptable for the development of cyclic separation processes such as the PSA process. The sorption hierarchy for the C_6 isomers follows the order of their boiling points, however the rise in of the temperature cause a displacement of the C_5 alkanes breakthrough curves relatively to the C_6 ones. Such effect is mainly due to the fact that adsorption enthalpies of C_5 alkanes are significantly lower than for C_6. Consequently, Figure 2b shows that is possible to separate a high RON fraction composed by 22DMB, iPEN and 23DMB from a 6-component mixture at the optimum temperature 583 K. Figure 2c shows the breakthrough curves of a simulated light naphtha fraction at 473 K. The quality of the hydrocarbon mixture obtained is around 88 RON if the adsorption step is cut just before 3MP leaves the column representing a slight increase comparatively with the conventional isomerization processes. Further experiments will be focused on improving the operating conditions in order to establish if zeolite BETA can be a valuable alternative for zeolite 5A in the separation of alkane isomers by cyclic processes.

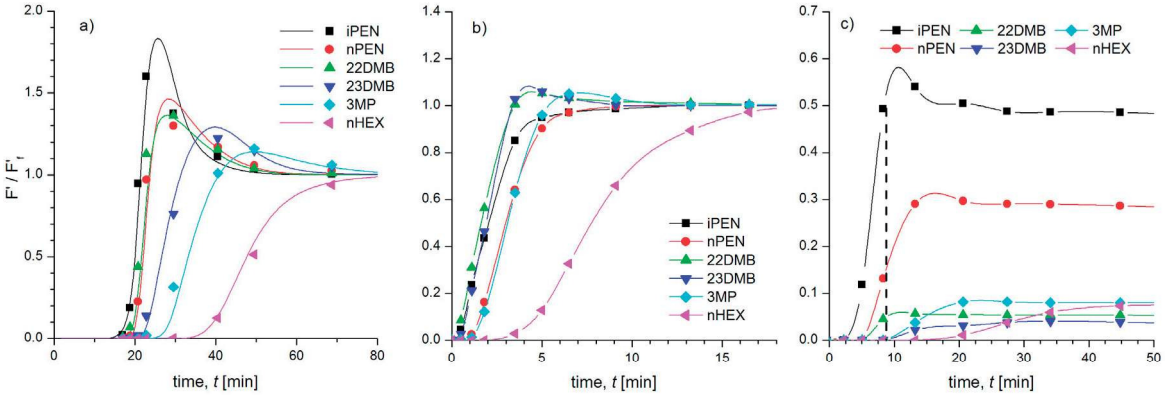

Figure 2. 6-component breakthrough curves at p_{mix}=10 kPa: a) equimolar at 423K; b) equimolar at 583K and c) molar composition of stream [2] in Figure 1b at 473 K. Lines in a) are the dynamic mathematical model simulation using the Tri-site Langmuir model predictions. Lines in b) and c) are to aid the eyes.

Acknowledgements

Bárcia P.S. acknowledges a grant from Fundação para a Ciência e Tecnologia (FCT) (SFRH/BD/30994/2006). Silva J.A.C. acknowledges financial support from FCT under project EQU/60828/2004.

References

1. Bárcia PS, Silva JAC, Rodrigues AE, AIChE J., 53 (2007), 1970-1981.
2. Holcombe TC, Sager TC, Volles WK, Zarchy A. Isomerisation Process, U.S. Pat. 4,929,799, 1990.